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The Solubility of Electrodeposited Tc(IV) Oxides

R. E. Meyer
W. D. Arnold
F. I. Case

Prepared for the
U.S. Nuclear Regulatory Commission
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R. E. Meyer
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ABSTRACT

Solubilities of electrodeposited Tc(IV) oxides have been determined in solutions of NaCl, HCl, and synthetic groundwater in the pH range 0 to 10. Oxides were electrodeposited onto platinum electrodes, and the oxide-covered platinum was then placed into a small stirred cell. Solubilities were determined by counting the beta radiation of ^{99}Tc in the solution in the stirred cell. The solubilities are approximately constant in the pH range 3 to 10; the values in this region for deposits from acid solution average $(1.32 \pm 0.68) \times 10^{-8}$ mol/L. For oxides deposited from basic solutions the average is $(2.56 \pm 0.54) \times 10^{-9}$ mol/L. The electrodeposited oxides are hydrated and experiments show that they have the composition $TcO_2 \cdot nH_2O$ where n has an average value of 1.63 ± 0.28. The oxides appear to vary in structure and/or composition depending on their method of preparation and history. Solubility products between 10^{-32} and 10^{-33} can account for most of the data. These data can be used to estimate solubilities for cases where solubility limits transport of technetium in reducing high-level waste repository environments.

CONTENTS

	Page
ABSTRACT	iii
LIST OF FIGURES AND TABLES	vii
EXECUTIVE SUMMARY	ix
1. INTRODUCTION	1
2. BACKGROUND	1
2.1 Electrode Potentials	2
2.2 Hydrolysis Reactions	3
2.3 Solubility	4
3. EXPERIMENTAL	7
3.1 Introduction to Experimentation	7
3.2 Procedures	7
3.2.1 Maintenance of Anoxic Conditions	7
3.2.2 Valence State Determination	7
3.2.3 Electrodeposition of Tc(IV) oxide	8
3.2.4 Determination of Stoichiometric Formula of Tc(IV) Oxide	8
3.2.5 Procedure for Determination of Solubilities	9
3.3 Results	9
4. DISCUSSION	11
5. SUMMARY AND CONCLUSIONS	15
6. PLANS FOR FURTHER EXPERIMENTATION	16
7. REFERENCES	17

LIST OF FIGURES

Figure | Page

1. Total concentration of Tc(IV) species in equilibrium with precipitated oxide vs pH. Column determination using oxide precipitated onto purified sand. Line drawn with Ksp = 10^{-32} (from Meyer et al. 1986) 5

2. Total concentration of Tc(IV) species in equilibrium with electroreduced oxide vs pH. Line drawn with Ksp = 10^{-33} (from Meyer et al. 1986) 6

3. Concentration of TcO_4^- vs Eh. pH 1.9, 0.1 M NaCl, E_0 = 0.738 V (from Meyer et al. 1986) 13

4. Total concentration of Tc(IV) species in equilibrium with electroreduced oxide vs pH. Line drawn with Ksp = 10^{-33} 14

LIST OF TABLES

Table

1. Solubilities of Electrodeposited Tc(IV) Oxides 10

2. Determination of Stoichiometry of Tc(IV) Oxide (values of n in formula $TcO_2 \cdot nH_2O$) 11

EXECUTIVE SUMMARY

Solubilities of electrodeposited Tc(IV) oxides have been determined in solutions of NaCl, HCl, and synthetic groundwater in the pH range 0 to 10. Oxides were electrodeposited onto platinum electrodes, and the oxide-covered platinum was then placed into a small stirred cell. Solubilities were determined by counting the beta radiation of ^{99}Tc in the solution in the stirred cell.

The Tc(IV) oxides formed by electrodeposition are hydrated and have a composition of $TcO_2 \cdot nH_2O$ where n has an average value of 1.63. Solubilities of the oxides are approximately constant from pH 3 to 10; the values in this region for deposits from acid solutions average $(1.32 \pm 0.68) \times 10^{-8}$ mol/L. For oxides deposited from basic solutions the average is $(2.56 \pm 0.54) \times 10^{-9}$ mol/L. These data can be explained if the principal Tc(IV) aqueous species is neutral above pH 4. There appears to be a solubility minimum around pH 3.

In acid solutions, the behavior can be accounted for by assuming a hydrolysis scheme where doubly charged, singly charged, and neutral species are formed. Oxides aged in basic solution appeared to be less soluble than oxides freshly prepared in acidic solution.

The oxides appear to vary in structure and/or composition depending on their method of preparation and history. Solubility products between 10^{-32} and 10^{-33} can account for most of the data. Within the limits of the precision of the measurements, there were no significant differences in results in NaCl, BWIP synthetic groundwater GR-4, and pH 9.6 sodium carbonate solutions.

Because we have found a fairly reproducible solubility in basic solutions, this value represents a reasonable value to use for a maximum concentration of technetium in equilibrium with a precipitated oxide. Although this solubility is probably greater than that of well-formed anhydrous TcO_2, it is more reasonable to use the larger more conservative value for situations where solubility-limited transport rates are calculated for the purpose of safety assessment. Our values of 1.32×10^{-8} mol/L for acid-deposited oxides and 2.56×10^{-9} mol/L for base-deposited solutions are far larger than the value of 10^{-14} calculated for Eh = -0.3 V (Salter and Jacobs 1983) for the expected redox conditions in a basalt repository, but it is smaller than the conservative value of 10^{-5} mol/L given by BWIP (Salter and Jacobs 1983).

THE SOLUBILITY OF ELECTRODEPOSITED Tc(IV) OXIDES

R. E. Meyer, W. D. Arnold and F. I. Case

Oak Ridge National Laboratory
Oak Ridge, TN

1. INTRODUCTION

The nuclide ^{99}Tc, $t_{1/2}$ = 213,000 years, is present in large quantities in nuclear waste, and properties related to its migration in geological environments are therefore of considerable interest. Under oxidizing conditions, technetium is expected to exist in the (VII) valence state as the anion, TcO_4^-. In the event that technetium is released into the groundwater surrounding a geologic high level waste repository in the form of TcO_4^-, it is not expected to be adsorbed significantly on the minerals and rocks present because of its negative charge. A number of studies have confirmed that little or no sorption occurs under oxic conditions (Salter et al. 1981, Barney 1982, Barney 1983, Palmer and Meyer 1981). However, if the technetium is reduced to a lower valence state, then it is possible that species may be formed that either are more highly adsorbed or are insoluble enough to limit the maximum concentration of technetium in the groundwaters surrounding the repository. This solubility-limited concentration enters into the calculation of the release rate of technetium to the environment in the event that the repository is breached by groundwater. Other factors entering into this calculation are groundwater flow rate, length and nature of the path to the accessible environment, and possible dilution of the technetium-containing groundwater by non-contaminated groundwater. It is evident that the nature and solubility of reduced species of technetium compounds need to be known for the calculation of technetium releases from a repository in a reducing geological environment.

Based upon current knowledge of technetium chemistry, it is generally predicted that some form of Tc(IV) oxide will be formed if reducing conditions exist in a repository geological environment. However, technetium has an unusually complicated redox chemistry, and much is unknown about the chemistry of lower valence states. In particular, little is known about the solubilities of Tc(IV) oxides. Therefore, as part of our general study of the effects of valence and speciation on the migration properties of nuclides (Meyer et al. 1983, Meyer et al. 1984, Meyer et al. 1985, Meyer et al. 1986) we have studied the solubility of Tc(IV) oxides in pure solutions of NaCl and HCl and in synthetic groundwater formulations.

2. BACKGROUND

Because the chemistry of the oxy-compounds of technetium is extremely important to the safety analysis of technetium migration, a number of reviews have been written recently which deal with the chemistry and thermodynamics of technetium. A comprehensive review has been given by Rard (1982). This is probably the most complete review to date, and it has 240 references to technetium chemistry. In this work,

judgments are given as to the reliability of the reported data. Another recent review, which is less comprehensive but presents the pertinent chemistry relative to nuclear waste disposal, is that of Paquette et al. (1980). A critical review of the data on electrode potentials, solubilities, and hydrolysis of Tc(IV) species is given in Meyer et al. (1986).

To calculate solubilities, the solubility product needs to be known in addition to data for all species such as hydrolytic products in equilibrium with the solid. The thermodynamic data pertinent to calculation of solubilities are briefly summarized below.

2.1 Electrode Potentials

The only really generally recognized thermodynamic data are those concerning the potential of the equilibrium between TcO_2 and TcO_4^-, Eq. 2.1. The usual value quoted in the literature for the standard potential, 0.738 V, is that of Cartledge (1955).

$$TcO_2 + 2H_2O = TcO_4^- + 4H^+ + 3e^- \qquad E_0 = 0.738\ V \qquad (2.1)$$

Even this number is somewhat open to question because other investigators have obtained somewhat different results (Cobble et al. 1953, Spitsyn et al. 1964, and Liebscher and Munze 1975). Values found by Meyer et al. (1986) were within a few millivolts of 0.738 V. In these measurements, the method of formation of Cartledge was reproduced as exactly as possible. The solutions were analyzed for TcO_4^- and reduced states of Tc. Analyses for TcO_4^- and Tc(IV) are necessary for cases where the concentration of reduced technetium might be significant compared to the concentration of TcO_4^-. Such might be the case for acid solutions, where the concentrations of reduced technetium can be significant.

As pointed out by Isherwood (1985), the potential for the Tc(IV) - Tc(VII) couple (Eq. 2.1) probably refers to a hydrated oxide rather than the non-hydrated oxide, TcO_2. In a later publication, Cartledge (1971) refers to oxide electrodeposited by the method used in his 1955 determinations as the hydrated form, $TcO_2 \cdot 2H_2O$ or possibly $Tc(OH)_4$. Thus, thermodynamic calculations based on the 0.738 V potential should probably refer to the hydrated form of Tc(IV) oxide.

Using Equation 2.1, and, assuming a value of Eh for the repository environment, it is possible to calculate the amount of TcO_4^- in equilibrium with the solid Tc(IV) oxide. In this way, estimates of minimum solubilities of 10^{-12} to 10^{-14} mol/L have been obtained for the solubility of TcO_2 (Early et al. 1982, Salter and Jacobs 1983). Because there were no data available for the solubility of reduced oxides of technetium, this calculation makes no allowance for any aqueous species of Tc(IV) or technetium in other reduced valence states. For this reason, these values were given in these references as minimum solubilities. Calculations or measurement of the solubility of TcO_2 must take into account the presence in solution of all species of Tc, and the presence of reduced species could lead to solubilities considerably in excess of 10^{-12} mol/L.

2.2 Hydrolysis Reactions

To calculate the concentrations of Tc(IV) species in equilibrium with the solid oxide, the solubility product and hydrolysis constants must be known. Only a limited amount of such data has appeared in the literature.

Gorski and Koch (1969) have reported electromobility measurements from which they calculated equilibrium quotients for hydrolysis reactions which they write as follows:

$$TcO_2^+ + H_2O = TcO(OH)^+ + H^+$$
$$K_{h1} = 4.3 \times 10^{-2} \pm 0.4 \times 10^{-2} \qquad (2.2)$$

$$TcO(OH)^+ + H_2O = TcO(OH)_2 + H^+$$
$$K_{h2} = 3.7 \times 10^{-3} \pm 0.4 \times 10^{-2} \qquad (2.3)$$

Their experiments were done by measuring the ionic mobility of Tc(IV) in columns composed of sea sand using solutions of pH from 1 to 2.5. Their data showed sharp decreases in mobility at about pH 1.3 and 2.2. At pH values above about 2.3, the mobility was approximately zero, an observation which indicated an uncharged species. The height of the first step (pH 1 to 1.3) of the mobility vs pH curve was twice that of the second step (pH 1.3 to 2.2). This observation was taken as evidence of the migration of a doubly charged species in the first step and a singly charged species in the second step. The concentration of the technetium was not given. However, because ^{99}Tc was used as the tracer, it could have been in the range of 10^{-7} to 10^{-5} M. The starting material in this study is reported to be technetium dioxide hydrate ($TcO_2 \cdot H_2O$) which was freshly prepared by reduction of NH_4TcO_4 with hydrazine in a solution of perchloric acid. The hydrated dioxide was freshly prepared before each individual experiment because it is easily oxidized. If any significant fraction of the oxide had been oxidized to TcO_4^-, then reverse migration would have been observed in the column because of the negative charge of the TcO_4^- ion.

Since the hydrolysis studies of Gorski and Koch were reported, two reports of unsuccessful attempts to repeat it have appeared (Sundrehagen 1979, Noll et al. 1975). A critical discussion of these experiments was given in Meyer et al. (1986). It appears that an important factor in these experiments is the initial concentration of technetium. If the concentration is too high, polymeric and/or colloidal forms of technetium may be present.

Support for Gorski and Koch's results comes from the work of Owunwanne et al. (1977) who worked with carrier-free ^{99m}Tc at low concentrations (10^{-7} to 10^{-9} mol/L). Using standard ion exchange techniques, they determined a charge of plus two for the Tc(IV) species at pH values <2. Owunwanne et al. suggest, on the basis of correlations with the formal charge of the metal and the pH, that the species in their experiment was actually $Tc(OH)_2^{2+}$ or possibly a mixture of $Tc(OH)_2^{2+}$ and TcO^{2+}.

Sundrehagen (1979) reports hydrolysis constants from spectrophotometric measurements in the ultraviolet spectrum region for the reaction given in Eq. 2.3 and a constant for a dimerization reaction (Eq. 2.4)

postulated to account for the observation that their plot of molar absorbance with concentration was not constant.

$$2TcO(OH)_2 = (TcO(OH)_2)_2 \qquad (2.4)$$

The values for the constants are K_{h2} = (9.3±2.0) x 10^{-3}, and K_{dim} = (3.14±0.28) x 10^6. These values were obtained by a computer fitting routine of a plot of molar absorbance as a function of concentration of Tc(IV). The data were collected at 210 nm, a region in the ultraviolet spectrum where it is quite difficult to obtain reliable data. The dimerization reaction, Eq. 2.4, is postulated to account for the observation that the molar absorbance was constant above about 10^{-5} M Tc(IV) but increased rapidly below this concentration. If the assumption that the dimerization reaction occurs is valid, then the change of molar absorbance with concentration implies that above this concentration (10^{-5} mol/L), dimerization is essentially complete, but below this concentration, the monomer is formed. In addition, it was assumed that a singly charged species hydrolyzed (as in Eq. 2.3) to form the monomer. The constants obtained from this study were obtained from the data-fitting routine assuming the two reactions, Eqs. 2.3 and 2.4, to occur. These experiments were done in 0.028 M $HClO_4$ with added $NaClO_4$ and 0.05 M $HClO_4$ with enough $NaClO_4$ to maintain the same ionic strength. The data fitting routine did not produce a better fit when the first hydrolysis reaction (Eq. 2.2) was included. We have not seen any other spectroscopic study of this type or any confirmation of the spectrum at these wavelengths.

2.3 Solubility

On the basis of a single determination of solubility by Lefort (1963) and the data reported by Gorski and Koch (1969) and by Sundrehagen, Rard (1983) calculated a solubility product for $TcO_2 \cdot H_2O$, Log_{10} Kso = -33.45 ± 1.0 at infinite dilution.

Meyer et al. (1986) have reported solubility measurements of electrodeposited and precipitated Tc(IV) oxides. The electrodeposited oxides were deposited from acid solution onto a platinum gauze electrode using a procedure similar to that used by Cartledge (1955) for electrode potential measurements. The precipitated oxides were formed by reduction with hydrazine onto washed sea sand; the resulting product was placed into a column, and solution was recirculated through the column until the concentrations in solution reached equilibrium. The technetium in solution was composed of Tc(VII) in the form of TcO_4^- and reduced technetium, which was assumed to be Tc(IV). The TcO_4^- was removed by a solvent extraction technique and the reduced technetium was left in solution. There was always a small and variable amount of TcO_4^- in the solution, possibly formed by oxidation by radiolytic products. Results for the two methods of formation of technetium oxide are shown in Figs. 1 and 2. The solid curves are drawn by calculation from the hydrolysis constants of Gorski and Koch (1969) and a solubility product which assumes the solid to be $TcO(OH)_2$ according to the discussion of Rard (1982). Reasonable agreement is observed between the lines and the calculated curves with the assumed solubility products shown in the figure legends; the assumed values for the solubility products are close to the estimate, log_{10} Kso = -33.45 ± 1.0 given by Rard (1982).

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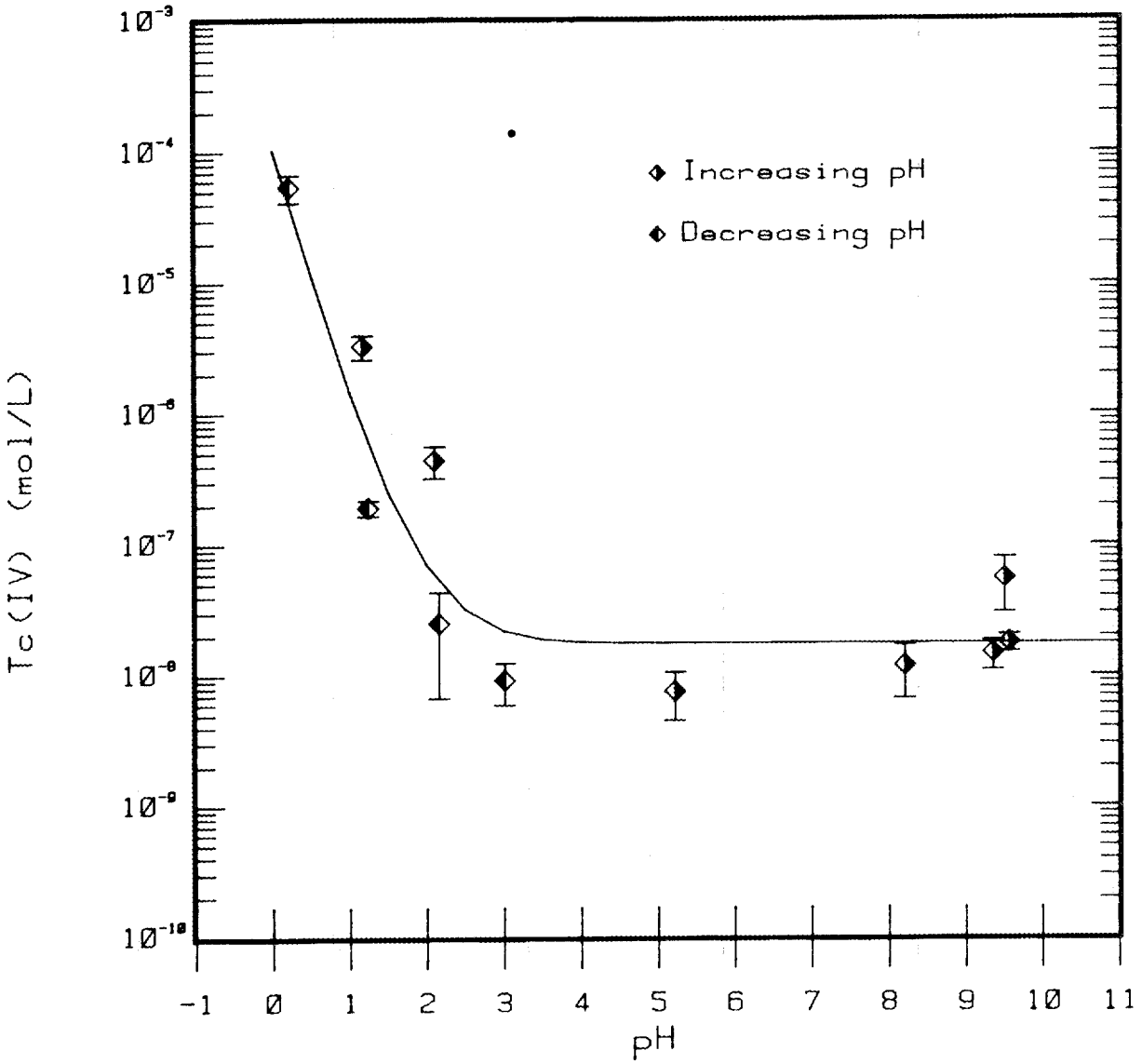

Fig. 1 Total concentration of Tc(IV) species in equilibrium with precipitated oxide vs pH. Column determination using oxide precipitated onto purified sand. Line drawn with Ksp = 10^{32} (from Meyer et al. 1986).

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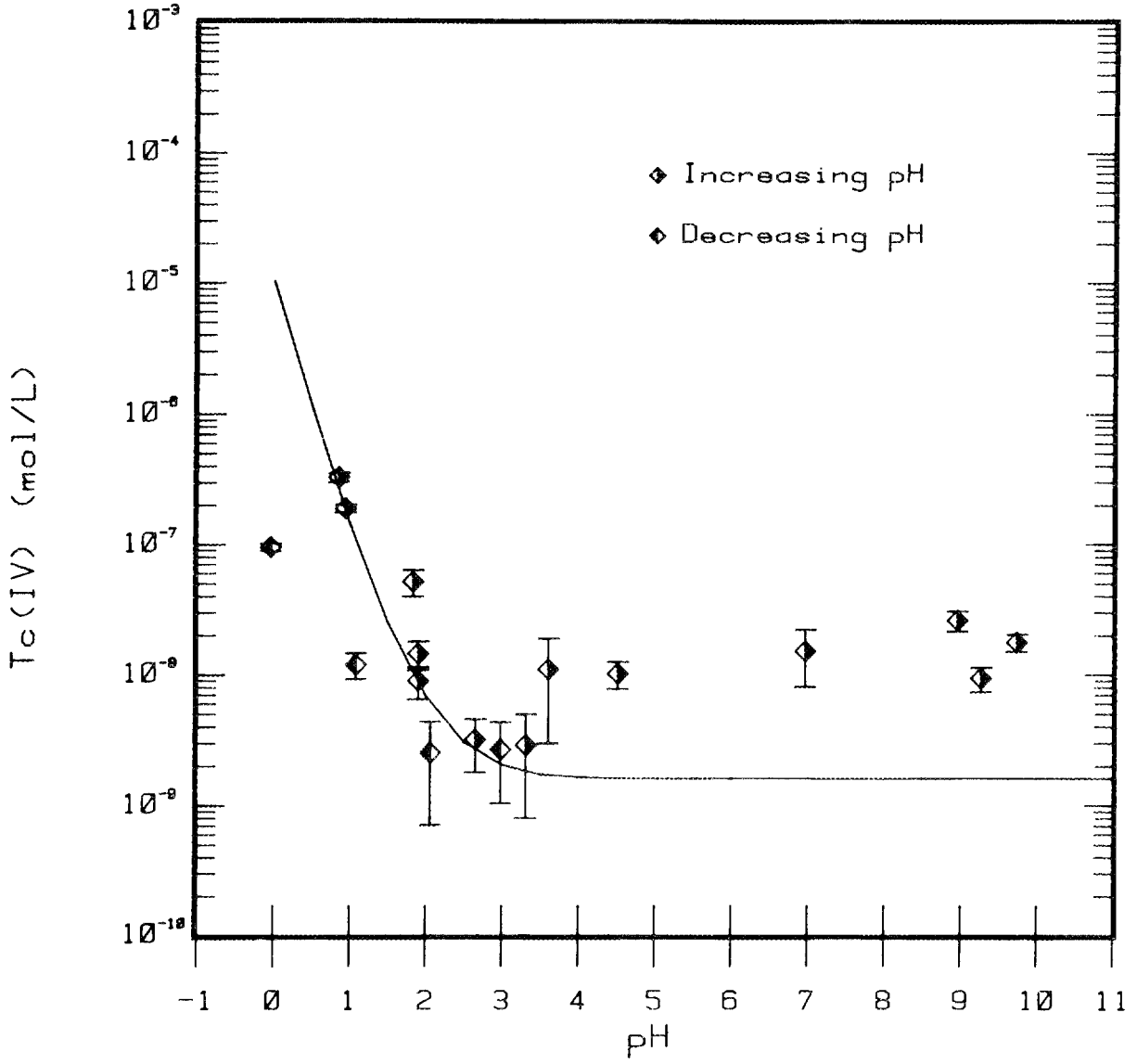

Fig. 2 Total concentration of Tc(IV) species in equilibrium with electroreduced oxide vs pH. Line drawn with Ksp = 10^{33} (from Meyer et al. 1986).

Although the precision of the experiments may not be sufficient to make a distinction of 1.0 in the $\log_{10}$ of the solubility product, there does appear to be a consistent difference between the oxides formed by electrodeposition and those formed by precipitation.

3. EXPERIMENTAL

3.1 Introduction to Experimentation

Determination of the concentration of Tc in equilibrium with Tc(IV) oxides is a difficult experiment at high pH levels because the concentration levels are low. Probably, the best practical method of determination of these low concentration levels is liquid scintillation counting of the beta emission of ^{99}Tc. Furthermore, Tc(IV) is easily oxidized, and experiments must be protected from oxygen and other possible oxidizing agents.

To lend more confidence to the data, several methods of preparing Tc(IV) oxides were used by Meyer et al. (1986). In the first of these, Tc(IV) oxide was formed by precipitation with hydrazine from a solution containing TcO_4^-. This is a procedure reported in the literature to produce $TcO_2 \cdot nH_2O$ (Gorski and Koch 1969, Sundrehagen 1979). When Tc(IV) oxide is precipitated from solution, it is generally believed that a hydrated form of the oxide is produced. The second procedure involves electrodeposition of Tc(IV) oxide from a solution of TcO_4^- (Cartledge 1955). With the third procedure, Tc(IV) oxide was precipitated with hydrazine on sand that had been carefully purified, and a column of the resulting material was placed in a recirculating loop of solution. For each procedure, the concentration of Tc in solution was monitored as a function of time. The solution was then centrifuged, and the centrifugate was then treated by solvent extraction to determine the concentration of reduced technetium. Each individual experiment was continued until measured concentration levels were constant within experimental error. In the work reported here, we have concentrated on electrodeposited oxide because this procedure enabled us to weigh the oxide more easily for estimation of the degree of hydration of the oxide.

3.2 Procedures

3.2.1 Maintenance of Anoxic Conditions

Because Tc(IV) is so easily oxidized, all operations were carried out in a controlled atmosphere box filled with high purity argon. The oxygen level in the argon was constantly monitored and was kept to levels on the order of 0.3 to 0.7 ppm. If levels greater than this were observed, the oxygen getter was regenerated. Sampling, centrifugation, and solvent extraction were carried out within the box. Exposure to air occurred only when the final samples were removed for counting.

3.2.2 Valence State Determination

The valence state of the species in equilibrium with Tc(IV) oxides must be determined for an accurate measure of the true solubility of the oxide. The procedure followed is one which we have used previously

(Meyer et al. 1986) to determine the valence state of adsorbed technetium on various minerals. The procedure consists of solvent extraction of the solution with tetraphenyl arsonium chloride dissolved in chloroform. The organic phase removes the TcO_4^- very efficiently, leaving reduced species in the solution. If the ratio of Tc(VII) to Tc(IV) is very high, two extractions are done to insure that all of the Tc(VII) is removed before determining the concentration of Tc(IV) in the solution.

3.2.3 Electrodeposition of Tc(IV) Oxide.

For the preparation of electrodeposited technetium, a large platinum mesh electrode was constructed and placed into a Princeton Applied Research (PAR) electrolytic cell which has a capacity of about 100 mL. The electrode has a cross-sectional area of about 6 cm^2. It is difficult to estimate the actual geometrical area of a mesh electrode; we estimate that the actual area is 3-4 cm^2. Enough of our stock solution was added to produce a solution of about 0.005 M Tc, and the pH was adjusted to about 2 with HCl. The potential imposed on the electrode by the potentiostat was gradually made more reducing, and significant electrolysis occurred at -200 mV vs the saturated calomel electrode (SCE). With respect to the hydrogen scale, the potential was +46 mV. The current density was approximately 1.0 mA/cm^2. A black solid gradually formed on the electrode, and after about two and a half hours, deposition was stopped. Oxides electrodeposited from alkaline solution were also studied. In this case the technetium was added to 0.01 M NH_4OH. The initial potential was much more negative and significant deposition did not occur until the potential was lowered to -850 to -900 mV vs the standard calomel electrode. As in the case of deposition from acid solution, a black deposit was formed, but it did not seem to adhere to the electrode as well as the oxides formed in acid solution.

3.2.4 Determination of Stoichiometric Formula of Tc(IV) Oxide

As described in Section 3.2.3, oxides were formed by electrodeposition on the large platinum electrode. To avoid oxidation of the technetium all operations were done within the controlled atmosphere box containing argon. Before electrodeposition, the electrode was carefully cleaned, dried and weighed (ca. 4 gm). It was placed into an electrodeposition cell containing ca. 5×10^{-3} M NH_4TcO_4 and either 0.01 M HCl or 0.01 M NH_4OH, and a deposit of from 10 to 25 mg was formed by electrodeposition. The electrode was then removed from the solution, rinsed carefully with distilled water and allowed to dry in the controlled atmosphere box. The moisture in the box atmosphere was continuously removed by circulation of the argon over molecular sieves. Thus the drying conditions were effectively 0% humidity at the temperature of the interior of the box, approximately 30°C. After a drying period, up to 7 days, the electrode was carefully wrapped in a weighed piece of aluminum foil. This was done to avoid any loss of oxide when the oxide-covered electrode was taken out of the box and weighed. The weight of the oxide was determined by difference. The amount of technetium in the oxide was then determined by dissolving the oxide with concentrated HNO_3, diluting the HNO_3 solution, and determining the technetium content of the diluted HNO_3 solution by

liquid scintillation counting of the ^{99}Tc.

As a check on the amount of technetium in the deposit, two further tests were conducted. The first was calculation of a material balance determined by measuring the loss of technetium from the original electrodeposition solution. The second was a measurement of the total charge in coulombs passed through the cell during the electroreduction of the technetium to form the oxide. For the latter measurement, a Princeton Applied Research (PAR) Model 179 digital coulometer was used with the PAR Model 173 Potentiostat/Galvanostat. Neither of these two methods is as accurate as the weight method described above, but these two alternate methods served as a rough check on the composition of the oxide. The material balance method suffers from the disadvantage that the technetium solution diffuses into the anode chamber through the porous frit separating the anode and cathode chambers; it was especially difficult to determine the amount of technetium that diffused through. The coulometric method had the disadvantage that the efficiency of electrolysis could not be assumed to be 100% because the electrode was changing as it became covered with oxide. Other electrode reactions could occur during the electrolysis, and therefore the actual efficiency could not be determined precisely.

3.2.5 Procedure for Determination of Solubility

Technetium solubility was measured in solutions in contact with electrolytically deposited Tc(IV) oxides. In a typical run, one mL samples were removed daily immediately after the pH was monitored. Each sample was then centrifuged at 14,000 rcf for 15 minutes. A 0.2 mL portion was saved as a head solution, and a 0.5 mL portion was treated by the solvent extraction process described above to distinguish between Tc(VII) and lower valence states, which we assume to be Tc(IV). The concentrations of ^{99}Tc were then determined in the 0.2 mL head solution and in the aqueous and organic phases from the valence state determination. A material balance was then calculated by comparing the total amount of technetium present as calculated from the head solution and the sum of the technetium from the organic and aqueous phases from the solvent extraction procedure. If the material balance was satisfactory, the concentrations of Tc(VII) and Tc(IV) in the original reservoir were calculated.

3.3 Results

Typically, for a given set of conditions, solubility values constant to within experimental error were achieved in a few days. To insure that steady state was achieved, the duration of each experiment was two weeks, and samples were taken almost daily. The solutions resulting from these experiments were analyzed by liquid scintillation counting as described above. In practice, for our apparatus this technique has a concentration limit (sensitivity) in the range of 10^{-9} to 10^{-10} mol/L Tc. At these concentration levels, the counts due to the technetium are of the same order of magnitude as the background count. Consequently, in our reported concentrations, we report much higher standard deviations for concentrations in this range. The results of the solubility determinations are shown in Table 1; concentration levels are determined by averaging the last five determinations before the

experiment was ended. Standard deviations from the calculations of these averages are also shown in Table 1.

Table 1. Solubilities of Electrodeposited Tc(IV) Oxides

Exp. #	Solution	pH	Reduced Tc (mol/L)	Std. Dev.	Log. Red. Tc
DEPOSITED FROM ACID SOLUTION:					
Tc-46	0.1 M HCl	0.85	3.30×10^{-7}	2.70×10^{-8}	-6.48
Tc-45	0.1 M HCl	0.94	1.90×10^{-7}	1.30×10^{-8}	-6.72
Tc-43	0.01 M HCl	1.83	5.20×10^{-8}	1.20×10^{-8}	-7.28
Tc-43	0.01 M HCl	1.90	9.00×10^{-9}	2.50×10^{-9}	-8.05
Tc-43	0.01 M HCl	1.90	1.45×10^{-8}	3.60×10^{-9}	-7.84
Tc-49	0.01 M NaCl	2.65	3.20×10^{-9}	1.40×10^{-9}	-8.49
Ascending pH - pH>3					
Tc-50	0.01 M NaCL	3.31	2.90×10^{-9}	2.10×10^{-9}	-8.54
Tc-51	0.01 M NaCl	3.60	1.10×10^{-8}	8.00×10^{-9}	-7.96
Tc-57	0.01 M NaCl	4.51	1.02×10^{-8}	2.40×10^{-9}	-7.99
Tc-61	0.01 M NaCl	6.97	1.52×10^{-8}	7.10×10^{-9}	-7.82
Tc-63	0.01 M NaCl	8.96	2.61×10^{-8}	4.60×10^{-9}	-7.58
Tc-65	GR-4	9.27	9.40×10^{-9}	2.00×10^{-9}	-8.03
Tc-67	0.01 M $NaHCO_3$*	9.74	1.77×10^{-8}	2.70×10^{-9}	-7.75
	Average for pH > 3:		1.32×10^{-8}		
	Std.Dev.:		6.81×10^{-9}		
Descending pH					
Tc-69	0.01 M NaCl	2.98	2.70×10^{-9}	1.66×10^{-9}	-8.57
Tc-73	0.01 M NaCl	2.06	2.55×10^{-9}	1.84×10^{-9}	-8.59
Tc-75	0.01 M NaCl	1.08	1.20×10^{-8}	2.70×10^{-9}	-7.92
Tc-77	1 M HCl	-0.04	9.58×10^{-8}	6.40×10^{-9}	-7.02
DEPOSITED FROM BASIC SOLUTION:					
Tc-88	GR-4	9.40	2.94×10^{-9}	2.80×10^{-9}	-8.53
Tc-89	0.01 M NaCL	8.73	2.76×10^{-9}	2.95×10^{-9}	-8.56
Tc-90	0.01 M NaCl	7.48	3.20×10^{-9}	1.69×10^{-9}	-8.49
Tc-91	0.01 M NaCl	5.62	1.70×10^{-9}	1.29×10^{-9}	-8.77
Tc-92	0.01 M NaCl	5.38	2.20×10^{-9}	7.77×10^{-10}	-8.66
	Average:		2.56×10^{-9}		
	Std. Dev.:		5.41×10^{-10}		

*Enough sodium carbonate added to bring pH to 9.74

The first determinations were done in acid solutions; subsequent determinations were done in basic solutions. In general, the same oxide was used for successive experiments; periodically the electrode was cleaned and a fresh deposit made. The experiments labeled 'Descending

pH' were done using the oxide that had been deposited immediately before experiment Tc-61. This oxide was then used for all subsequent runs through Tc-77. It had been exposed to several basic solutions and then to increasingly acid solutions. As shown, the results were lower in acid solution for electrodeposited oxides exposed to basic solution compared to electrodeposited oxides that had only been in acid solutions. Solubilities for oxides deposited in basic solution were about a factor of 5 lower than those deposited from acid solutions.

A summary of all of the determinations of the stoichiometry of Tc(IV) oxide is given in Table 2. It is assumed that the technetium oxide has the formula $TcO_2 \cdot nH_2O$. Values of "n" from both the weight method and coulometric method are given. The methods used to calculate these values and the errors involved are discussed below.

Table 2. Determination of stoichiometry of Tc(IV) oxide (values of n in formula $TcO_2 \cdot nH_2O$)

Run #	Drying time	n coulombic*	n by weight
Deposited from acid solution:			
Tc-78	2 hr	3.13	4.22
Tc-79	1 d	2.05	2.87
Tc-80	2 d	0.03	0.44
Tc-82	7 d	1.78	2.10
Tc-83	7 d	1.28	1.50
Deposited from basic solution:			
Tc-84	7 d	0	1.38
Tc-85	4 d	0.56	1.81
Tc-86	4 d	0.71	1.38

*Values of "n" determined by the coulombic method served only as a rough check. Values of "n" determined by weight are the most accurate.

4. DISCUSSION

The results shown in Table 2 demonstrate that Tc(IV) oxide formed by electrodeposition is hydrated. The average value of "n" for those dried 4 days or longer is 1.63 ± 0.28. This suggests that "n" may be two, but the precision of the experiment is not sufficient at present to determine a better value. This measurement is very sensitive to errors in the determination of the weight of the oxide. A total error of 0.0002 mg can produce an error of about 0.1 in the determination of "n". It may be possible to improve the reproducibility by improvements in the technique, e.g. by using a more sensitive balance and an electrode of much less weight than that used (ca. 4 gm). However, it is possible that there is no precise formula for the oxide and that the oxide is

amorphous with a somewhat indeterminate amount of water which will depend on many factors such as the precise drying conditions and the method of formation.

In the calculation of "n" it is assumed that all of the technetium present is in the (IV) oxidation state. To confirm this, electrochemical studies were carried out and reported in last year's report (Meyer et al. 1986) to insure that the reaction is that conforming to Eq. 2.1. By measuring the dependence of the potential on the concentration of TcO_4^- in solution, a confirmation can be made of the absolute value of the potential and the number of electrons involved in the potential-determining reaction. In Fig. 3, this relation is shown. The potentials were within a few mV of that calculated from Eq. 4.2 using the value of the standard potential, E_o = 0.738 V, determined by Cartledge (1955) in Eqs. 4.1 and 4.2 (based on Eq. 2.1).

$$E = E_o + (2.303\ RT/nF)\ \log[TcO_4^-][H^+]^4 \qquad (4.1)$$

$$E = 0.738 + (0.0197)\ \log[TcO_4^-] - 0.0788\ pH \qquad (4.2)$$

In this calculation, n = 3 and 2.303 RT/F = 0.0591 V. Cartledge reported a spread of 10 mV between his highest and lowest value of E_o. Thus this difference of a few mV between our measurement and the values calculated using E_o = 0.738 V is not surprising. The agreement between our values and values calculated from Eq. 4.2 confirms the three electron reduction to Tc(IV). In this experiment, the solubility of the solid phase (Tc(IV) oxide) can be significant relative to the concentration of TcO_4^-, and it is therefore important to make sure that the determination of the concentration of TcO_4^- is accurate and that the determination distinguishes between the concentration of Tc(IV) aqueous species and TcO_4^-. In Cartledge's work the concentrations of TcO_4^- were high enough that the limited solubility of Tc(IV) oxide could be safely ignored.

The results of the solubility experiments shown in Table 1 are plotted in Fig. 4 where the data are compared to theoretical lines calculated from solubility and hydrolysis data given in Eqs. 4.3 to 4.6. These equations follow the solubility discussion given by Rard (1982). In Rard's discussion the solid is assumed to be $TcO(OH)_2$ which corresponds to $TcO_2 \cdot H_2O$. We have modified Rard's equations slightly to show the oxide as $TcO_2 \cdot nH_2O$ and the divalent species as $Tc(OH)_2^{2+}$; in our experiments, n has an average value of 1.63±0.28.

$$TcO_2 \cdot nH_2O(solid) + (2-n)H_2O = Tc(OH)_2^{2+} + 2(OH)^- \quad Ksp\ (see\ Fig.\ 4) \qquad (4.3)$$

$$Tc(OH)_2^{2+} = TcO(OH)^+ + H^+ \quad K_{h1} = 4.3\times10^{-2} \qquad (4.4)$$

$$TcO(OH)^+ + H_2O = TcO(OH)_2(aqueous) + H^+ \quad K_{h2} = 3.7\times10^{-3} \qquad (4.5)$$

$$2TcO(OH)_2(aq.) = (TcO(OH)_2)_2(aq.) \quad K_{dim} = 3.14\times10^{6} \qquad (4.6)$$

This scheme assumes the existence in solution of neutral monomers and dimers of $TcO(OH)_2$. The concentration of $Tc(OH)_2^{2+}$ was calculated from the assumed value of Ksp and the pH using Eq. 4.3. Eqs. 4.4 to 4.6 were

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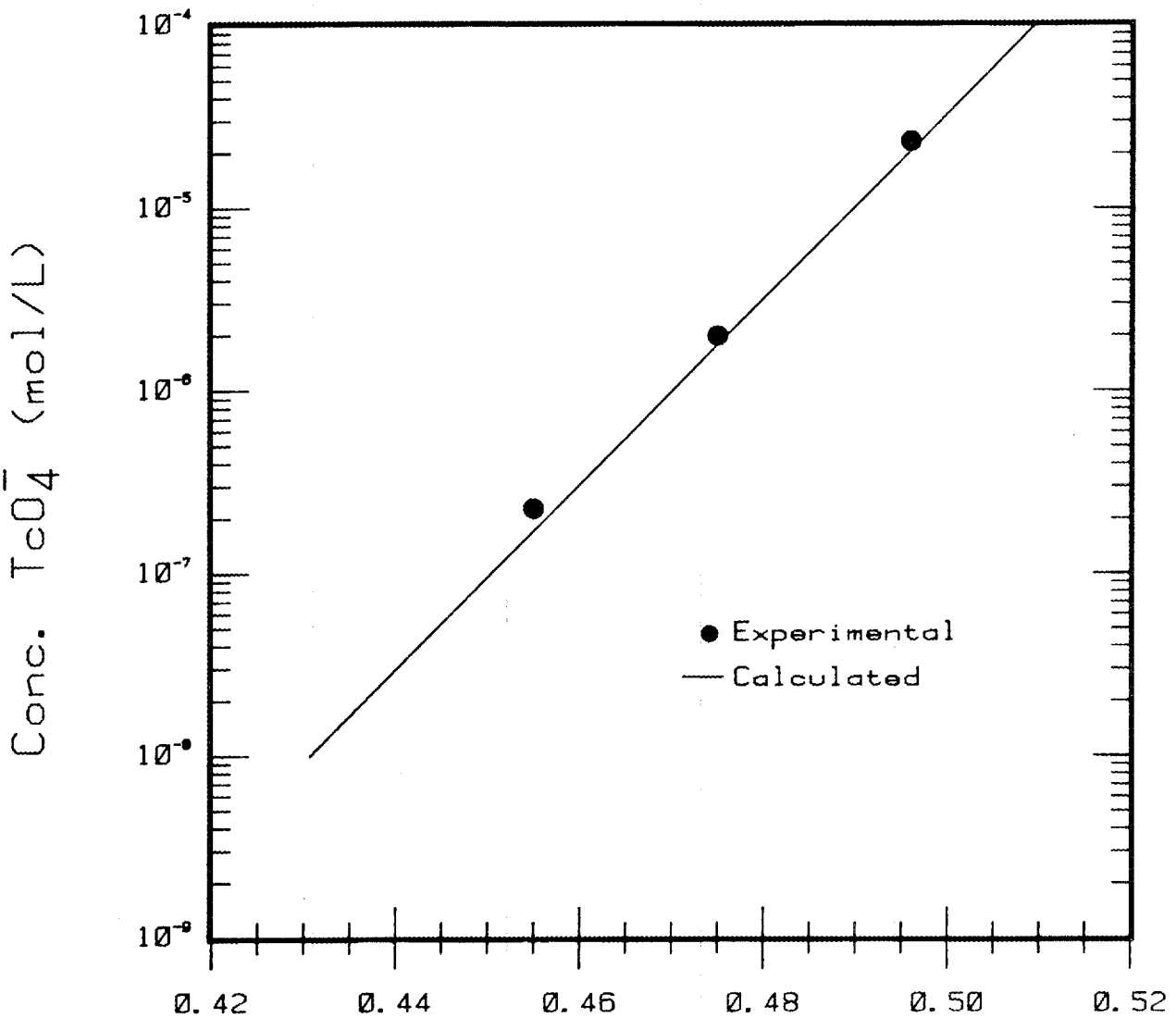

Fig. 3 Concentration of TcO_4^- vs Eh. pH 1.9, 0.1 M NaCl, E_0 = 0.738 V (from Meyer et al. 1986).

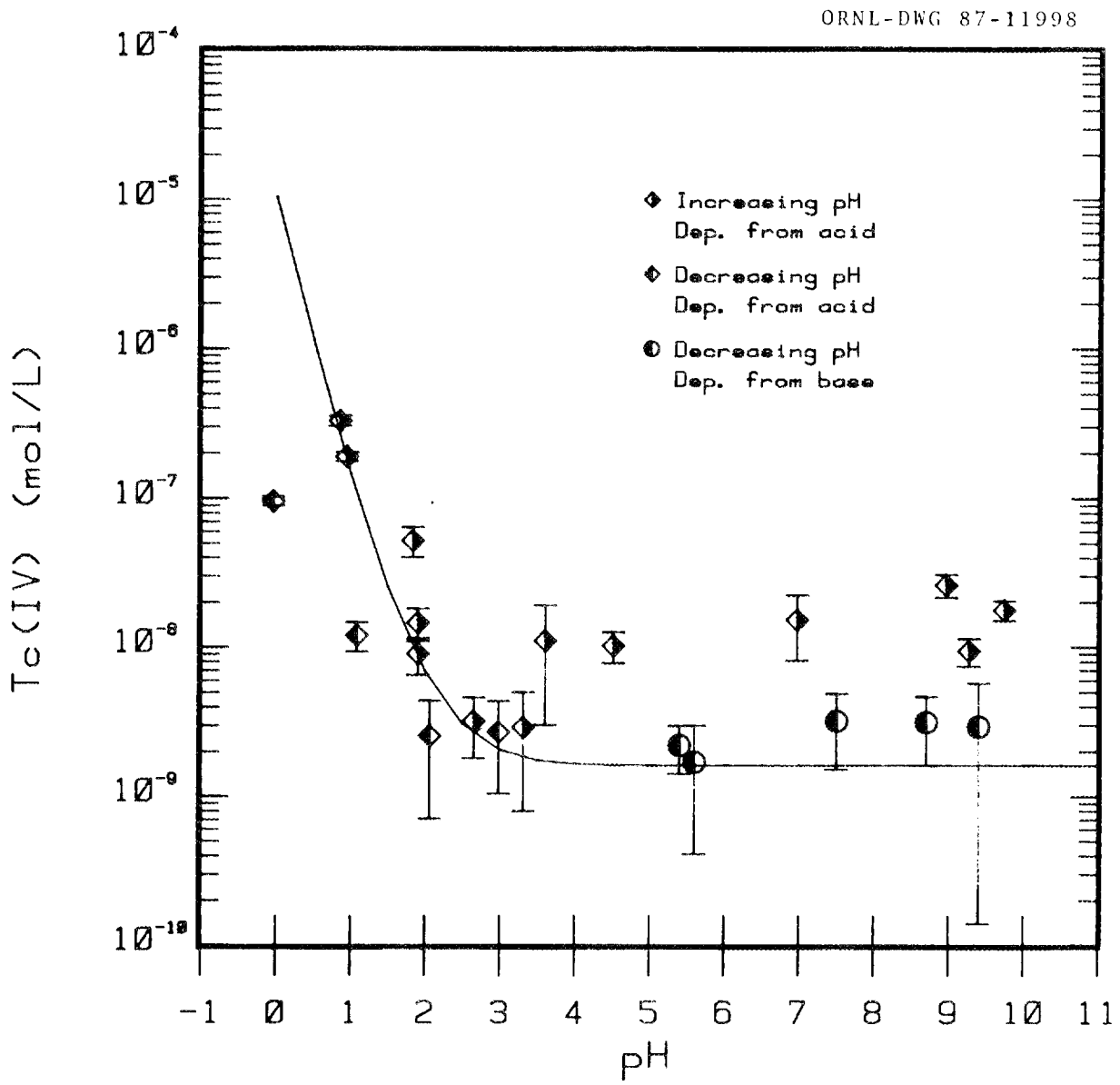

Fig. 4 Total concentration of Tc(IV) species in equilibrium with electroreduced oxide vs pH. Line drawn with Ksp = 10^{33}.

then used successively to calculate the concentrations of the other species.

Most of the solubility experiments were performed in solutions of HCl or NaCl which were adjusted to the indicated pH with either HCl or NaCl made basic by electrolysis. One experiment (Tc-65) was done in BWIP synthetic groundwater formulation GR-4 (Salter 1984), and experiment Tc-67 was done in a solution that was 0.01 M in $NaHCO_3$ and adjusted to pH 9.74. At this pH value, carbonate is present both as the bicarbonate and carbonate ions. Within the precision of the measurements at these pH values, there are no significant differences between the solubilities measured in NaCl, GR-4, and the carbonate solutions.

The general behavior of the experimental points in Fig. 4 suggests approximate agreement with the solubility scheme given in Eqs. 4.3 to 4.6. The experiments were done first in acid solutions, then in progressively more alkaline solutions, and then again in the acid solutions. In the second series of determinations in acid solutions, starting with Tc-69 at pH 2.98, the solubilities were lower than those determined in the first series done in acid solutions. These differences suggests that the oxide is changed when it is cycled through exposure to alkaline solutions and brought back to acid solution. Perhaps the initial oxide is amorphous and hydrated and as the oxide is equilibrated in alkaline solution it becomes more ordered and less hydrated. The data are not accurate enough or precise enough to justify any type of curve fitting. However, a Ksp = 10^{-33} appears to give fairly good agreement with the values observed in acid solution.

The differences in solubility between the first and second determinations in acid correspond to about a factor of ten in the solubility product. Differences in the structure and/or degree of hydration could account for these differences. The formula for Tc(IV) oxide has been variously reported as TcO_2, $TcO_2 \cdot H_2O$, $TcO_2 \cdot 2H_2O$, and $Tc(OH)_4$. To our knowledge there are no structure determinations by diffraction techniques although there are reports of electron diffraction patterns (Cartledge 1971).

5. SUMMARY AND CONCLUSIONS

(a) The Tc(IV) oxides formed by electrodeposition are hydrated and have a composition of $TcO_2 \cdot nH_2O$, where n has an average value of 1.63 ± 0.28.

(b) Solubilities of electrodeposited oxides are approximately constant from pH 3 to 10; the values in this region for deposits from acid solutions average $(1.32 \pm 0.68) \times 10^{-8}$ mol/L. For oxides deposited from basic solutions the average is $(2.56 \pm 0.54) \times 10^{-9}$ mol/L. These data can be explained if the principal Tc(IV) aqueous species is neutral above pH 4. There appears to be a minimum in solubility around pH 3.

(c) In acid solutions, the behavior can be accounted for by assuming a hydrolysis scheme according to Eqs. 4.3 to 4.6, where doubly charged, singly charged, and neutral species are formed. At pH 0, solubilities of from 10^{-7} to 10^{-4} can be expected depending on the nature of the oxide. Oxides aged in basic solution appear to be less soluble than oxides freshly prepared in acid solution.

(d) The oxides appear to vary in structure and/or composition depending on their method of preparation and history. Solubility products between 10^{-32} and 10^{-33} can account for most of the data.

(e) Within the limits of the precision of the measurements, there were no significant differences in results in NaCl, BWIP synthetic groundwater GR-4, and pH 9.6 sodium carbonate solutions.

The variability that we have observed in the solubility measurements, particularly in acid solutions, can be explained if the oxides that we have prepared change with time and exposure to the solution. If the oxides are amorphous and extensively hydrated initially but gradually tend toward less hydration and more order we would expect decreases in solubility. These decreases occur in acid solution but the measurements in basic solution seem relatively constant with time. This suggests a reproducible structure in basic solution.

Because we have found a fairly reproducible solubility in basic solutions, this value represents a reasonable value to use for a maximum concentration of technetium in equilibrium with a precipitated oxide. Although this solubility is probably greater than that of well-formed anhydrous TcO_2, it is more reasonable to use the larger more conservative value for situations where solubility-limited transport rates are calculated for the purpose of safety assessment. Our values of 1.32×10^{-8} mol/L for acid-deposited oxides and 2.56×10^{-9} mol/L for base-deposited solutions are far larger than the value of 10^{-14} calculated for Eh = -0.3 V (Salter and Jacobs 1983) for the expected redox conditions in a basalt repository, but it is smaller than the conservative value of 10^{-5} mol/L given by BWIP (Salter and Jacobs 1983).

7. PLANS FOR FURTHER EXPERIMENTATION

In view of the variability of solubility in acid solution, more information is needed on the degree of hydration and structure of the oxides. To extend these measurements to other conditions it is planned to extend these measurements to higher temperatures and to solutions of higher chloride content.

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ABSTRACT

Solubilities of electrodeposited Tc(IV) oxides have been determined in solutions of NaCl, HCl, and synthetic groundwater in the pH range 0 to 10. Oxides were electrodeposited onto platinum electrodes, and the oxide-covered platinum was then placed into a small stirred cell. Solubilities were determined by counting the beta radiation of ^{99}Tc in the solution in the stirred cell. The solubilities are approximately constant in the pH range 3 to 10; the values in this region for deposits from acid solution average $(1.32 \pm 0.68) \times 10^{-8}$ mol/L. For oxides deposited from basic solutions the average is $(2.56 \pm 0.54) \times 10^{-9}$ mol/L. The electrodeposited oxides are hydra- ted and experiments show that they have the composition $TcO_2 \cdot nH_2O$ where n has an average value of 1.63 ± 0.28. The oxides appear to vary in structure and/or composition depending on their method of preparation and history. Solubility products between 10^{-32} and 10^{-33} can account for most of the data. These data can be used to estimate solubilities for cases where solubility limits transport of technetium in reducing high-level waste repository environments.

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